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<b>(21) International Application Number:</b> PCT/US93/01846 <b>(22) International Filing Date:</b> 1 March 1993 (01.03.93)  <b>(30) Priority data:</b> 07/843,218 28 February 1992 (28.02.92) US  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 843,218 (CIP) Filed on 28 February 1992 (28.02.92)  <b>(71)(72) Applicant and Inventor:</b> DUGGER, Cortland, O. [US/ US]; 12600 Westover Ct., Upper Marlboro, MD 20772 (US).		<b>(74) Agents:</b> WHITE, John, L. et al.; Millen, White, Zelano & Branigan, Arlington Courthouse Plaza I, Suite 1400, 2200 Clarendon Boulevard, Arlington, VA 22201 (US).  <b>(81) Designated States:</b> CA, JP, KR, KZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> PRODUCTION OF TRANSPARENT CATIONICALLY HOMOGENEOUS REFRACTORY OXIDES OF NANOMETER-SCALE PARTICLE SIZE DIAMETERS AT REDUCED TEMPERATURES  <b>(57) Abstract</b>  Pure known and novel refractory oxides in a novel cationically homogeneous crystalline form with particle size diameters in the nanometer (< 100nm) range, which ordinarily are transparent and which can have one or both of electrostatic and magnetic properties due to the nanometer size diameters of its particles, can be produced by the successive steps of heating a hydrated halide or a hydrated halide-oxide mixture containing the metal cation or cations of the refractory oxide, homogeneously dispersed in a colloidal-like state, to a temperature at which a solid state hydroxyhalide complex containing only the cation or cations of the refractory oxide is produced; which complex when it is fully formed is then heated to a higher temperature until converted to a solid state oxyhalide complex; which complex when it is fully formed is then heated to a higher temperature until converted to a solid state metastable activated oxyhalide complex; which complex when it is fully formed is then heated to a higher temperature at which it is converted to the novel cationically homogeneous refractory oxide end product.		

**PRODUCTION OF TRANSPARENT CATIONICALLY HOMOGENEOUS  
REFRACTORY OXIDES OF NANOMETER-SCALE PARTICLE SIZE  
DIAMETERS AT REDUCED TEMPERATURES**

**Background of the Invention**

5           This invention relates to a novel process, hereinafter  
called the Uniform Cation Distribution Process (UCDP), for  
the manufacture at reduced temperatures of refractory  
oxides in a novel cationically homogeneous nanometer-scale  
particle size diameter physical form and to the novel  
10 products thereof.

          More particularly, this invention relates to a process  
for the manufacture, in from small to commercial size quan-  
tities, of refractory oxides in all compositional cate-  
gories including undoped, doped, solid solution, congruent  
15 melting, incongruent melting, stoichiometric and non-  
stoichiometric compositions as three-dimensional single  
crystals, polycrystals or glass entities, by thermochemical  
reactions of hydrated homogeneously dispersed colloidal-  
like mixtures of halides or halide-oxides to form and  
20 decompose (pyrolyze) metastable precursor complexes to end  
product entities. It also relates to the novel forms of  
known and novel refractory oxides and hydroxyhalide and  
oxyhalide complex thereto intermediates thereto which are  
produced by the process of this invention as well as the  
25 novel chemicals themselves.

Prior art halide hydrolysis as most frequently practiced consisted principally of crystallizing small, thin, stoichiometric, binary oxide single crystals from programmed temperature-cooled solutions. The purity and quality of the resultant crystals were poor mainly because of inevitable solvent inclusions in the crystals and the very low acceptable crystal yields were seldom reproducible due to indeterminate and insufficient water-volumes for complete thermochemical hydrolysis of metal halides.

Some references describing thermohydrolytic prior art procedures for synthesizing refractory oxide compounds are exemplified by the following:

1. Buerger, M.J., "The Structure Of The Mineralizer Action On Fluorine And Hydroxyl," The American Mineralogist, Vol. 33, 1948, p. 744.
2. Popov, A.I.; Knudson, G.E., "Preparation and Properties of the Rare Earth Fluorides and Oxyfluorides," J. Am. Chem. Soc., 76, Feb. 1954, p. 3921. p. 341.
3. Brixner, L.H., "Ferromagnetic Material Produced From Ferric Oxide And Barium Halide or Strontium Halide, And Process For Making Same," U.S. Patent 3,113,109, Dec. 3, 1963.
4. Messier, D.R.; Pask, J.A., "Kinetics of High Temperature Hydrolysis of Magnesium Fluoride: II, Influence of Specimen Geometry and Type and of Product Layers", J. Am. Cer. Soc., Vol 48, No. 8, Sept. 1965, p. 459.
5. Dugger, C.O., "The Growth of Pink Magnesium Aluminate ( $MgAl_2O_4$ ) Single Crystals," J. of Electrochem. Soc., Vol 113, No. 3, March 1966, p. 306.
6. Dugger, C.O., "Solution Growth of Oxidic Spinel and Other Oxide Single Crystals Following The Hydrolysis of Some Fluorides," J. of Phys. & Chem. of Solids Supplement, 1st Ed., Pergamon Press, New York, 1967, p. 493.

- 5           7. Cobb, C.M.; Wallis, E.B.; Investigation of the Solubility of Refractory Oxides in Fused Melts, The Dugger Crystal Growth Technique, and Factors Influencing the Growth of  $\text{Be}_2\text{GeO}_4$ , Final Report, AFCRL-69-0126, under Contract No. AF19628-67-C-0013, 21 March 1969.
8. Dugger, C.O., "Method For Growing Oxide Single Crystals," U.S. Patent 3,595,803, July 27, 1971.
- 10          9. Utsunomya, T.; Hoshino, Y.; Sato, M., "Process of Hydrolysis Reaction from  $\text{YF}_3$  to  $\text{Y}_2\text{O}_3$  in a Humid Air at High Temperatures," Bulletin of the Tokyo Institute of Technology, No. 108, 1972.

          Brixner, U. S. Patent No. 3,113,109, discloses a process for the production of a ferromagnetic refractory oxide material from ferric oxide and barium halide or strontium halide, in the presence of water vapor, oxygen or a mixture thereof, at 700-1350°C. In one aspect, a molten mixture of the ferric oxide and a 2-3 times stoichiometric excess of the metal halide is employed as the reaction medium. In such a technique, the cation composition of the reaction mixture differs from that of the mixed oxide product, i.e., the molar ratio of the metal of the metal halide is greater than its molar ratio in the refractory oxide product. Therefore, even though the product is in the form of single crystals, inherently the product is not cationically homogeneous because of occluded cations from the reaction medium, which differs in its cationic composition therefrom. Also, although transparent single crystals were obtained, they were in the form of thin substantially two dimensional platelets (10-100 microns thick and up to 2 mm in diameter) rather than three-dimensional, e.g., cubic crystals of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  produced according to the process of this invention measuring about 2 mm on each side. The process performed without a reaction medium, i.e., employing only with reactants corresponding stoichiometrically to the desired refractory oxide, employs a stream of oxygen. Such a process, while feasible on a laboratory

scale, is not feasible on a commercial production scale because it is not feasible or possible to ensure uniform contact of the reactants throughout the reaction mass with the reactant stream of oxygen. By employing a single  
5 cationically homogeneous oxyhalide which is pyrolytically convertible to the desired refractory oxide end product by heating alone, the process of this invention avoids the loss of reaction mass homogeneity during the production of the refractory oxide.

10 While the UCDP is a generic process for producing precisely high reproducible yields of all of the refractory oxide compositional categories, there is some scientific uncertainty as to the actual precursor (intermediate) reactions that occur in thermochemically converting a  
15 hydrated metal halide to a refractory oxide end product; only hydroxyhalide and oxyhalide complexes are reported in the literature. In addition, it is not certain if all hydrated metal halides convert to both intermediate complexes. For example, it is reported that, hydrated  
20 aluminum fluoride thermochemically forms only an aluminum hydroxyfluoride while hydrated yttrium fluoride forms only an yttrium oxyfluoride. Further, if the crystal structures of the hydroxyhalide and oxyhalide complexes are identical or similar, it is difficult to distinguish between the two  
25 complexes because of the almost identical  $\text{OH}^{-1}$  (1.33Å) and  $\text{F}^{-1}$  (1.34Å) ionic radii and the concentration range of each of these ions in a given structure. Thus, for generic explanatory purposes of this invention, it is assumed that all hydrated metal halides are thermochemically converted  
30 to both hydroxyhalides and oxyhalide complexes only and the hydroxyhalide and the oxyhalide complexes are considered to be low temperature ( $\leq 500^{\circ}\text{C}$ ) and high temperature complexes, respectively. Of course the intermediate solid state complex end products can be isolated only if they  
35 exist. Reactions I - IVB and the UCDP production procedure

f this invention are thus given.

#### Objects of the Invention

5 A primary object of this invention is to provide a novel process which can produce on a commercial scale substantially pure refractory oxides in novel physical forms and which have a homogeneous cation distribution, in a wide variety of compositional categories.

10 Another object is the provision of a process for the manufacture of such refractory oxides at temperatures ranging from 100°C to 1500°C below their pure melting points.

15 Still another object of this invention is to provide a process for producing in commercial amounts high purity transparent and nanometer-scale particle size diameter homogeneous refractory oxide compositions.

A further object of this invention is to provide a process which markedly reduces or eliminates the prior art disadvantages attendant to refractory oxide materials preparation.

20 Yet another object is the provision of novel cationically homogeneous crystals of known and novel substantially pure refractory oxides which are substantially three dimensional.

25 Yet another object is the provision of compositionally novel refractory oxides.

Still further objects of advantages and features of this invention will become apparent upon consideration of the following detailed description thereof.

#### Summary of the Invention

30 In a process aspect, this invention relates to a process which comprises producing and isolating a substantially pure cationically homogeneous metal oxyhalid which is pyrolytically convertible by heat alone to the

refractory oxide and then heating the isolated metal oxyhalide, in a reaction medium having a metal cation composition stoichiometrically identical to that of the refractory oxide, to a temperature at which the metal oxyhalide is converted pyrolytically to the corresponding homogeneous refractory oxide.

In a preferred aspect, the substantially pure cationically homogeneous metal oxyhalide is produced by the steps of (a) mixing with liquid water at least one metal halide, alone or in mixture with a metal oxide, which halide and oxide are convertible to a refractory oxide, or by mixing a refractory oxide with an aqueous hydrogen halide composition, to produce a homogeneous colloidal-like fully hydrated halide-oxide reactant mixture; and (b) heating the thus-produced hydrated halide-oxide reactant mixture to a temperature at which the refractory oxide end product is produced, optionally with isolation of one or both of the intermediately produced solid state hydroxyhalide complex and oxyhalide complex.

In another process aspect, this invention relates to a process for the manufacture of a substantially pure refractory oxide which has homogeneous cation distribution and particle size diameters in the nanometer range, at a temperature below the melting point of the refractory oxide, which comprises thermochemically hydrolyzing a dispersed homogeneous reaction mixture comprising a hydrated halide or hydrated halide-oxide to form usually sequentially through a plurality of thermally labile homogeneous precursor activated complexes, and sequentially thermochemically decomposing the intermediate complexes to a cationically homogeneous product by heating each complex to a higher temperature than the temperature at which the preceding complex was heated until the final precursor homogeneous complex decomposes into the desired homogeneous refractory oxide end product.

In another process aspect, this invention relates to a process for the production of a pure refractory oxide in a novel cationically homogeneous three dimensionally uniform crystalline form with particle size diameters in the nanometer (<100nm) range, at a temperature below the melting point of the pure refractory oxide, by the successive steps, of heating a fully hydrated halide or a hydrated halide-oxide mixture containing the metal cation or cations of the refractory oxide, homogeneously dispersed in a colloidal-like state, in an appropriate crucible, to a temperature at which a homogeneous solid state hydroxyhalide complex, containing only the cation or cations of the refractory oxide, is produced; it is then heated to its solid state hydroxyhalide metastable activated complex decomposition-temperature where it decomposes over time to a solid state homogeneous oxyhalide complex; it is then heated to its solid state oxyhalide metastable activated complex decomposition-temperature where it pyrolyzes over time to its novel cationically homogeneous refractory oxide end product; or, is heated to a still higher decomposition-temperature where the solid state oxyhalide complex becomes a molten oxyhalide complex and over time pyrolyzes to its novel cationically homogeneous refractory oxide end product; or, the molten decomposition-temperature is raised to a higher vapor phase decomposition-temperature where the molten oxyhalide complex vaporizes and pyrolyzes over time to its novel cationically homogeneous refractory oxide end product.

In a composition aspect, this invention relates to substantially pure cationically homogeneous refractory oxides in a novel substantially three dimensional crystalline form which have a particle size of less than 100 nanometers, most of which are transparent and many of which have one or both of electrostatic and magnetic properties.

In another composition aspect, this invention relates



to chemically novel refractory oxides.

In yet another composition aspect, this invention relates to the hydroxyhalide and oxyhalide precursor complexes to the refractory oxides of this invention.

5

#### Detailed Description of the Invention

The UCDP differs from the prior art refractory oxide manufacturing processes in that the refractory oxides are produced from a substantially pure uniform cationically homogeneous oxyhalide. The UCDP also differs in that it can produce on both large and small scales a wide variety of novel and known crystalline refractory oxides of all compositional categories from the three states of matter [solid, liquid (molten) and vapor phases] as substantially pure cationically homogeneous three dimensional transparent polycrystalline ceramic composites or single crystals.

15

The term "substantially pure" as used herein means the actual cationic composition thereof differs by no more than about 5 wt% from theoretical based upon wet chemical analysis, preferably less than 2 wt%, and most preferably, e.g., in the case of refractory oxides to be used in a laser or a superconductor, 0.25 wt% or less. The term "cationically homogeneous" means that the refractory oxide is substantially free of occluded extraneous cations, viz., as determined by X-ray powder diffraction. The term "refractory oxide" is used herein in its conventional sense. It is a metal oxide, usually with a plurality of metal cations and which has a fusion point, i.e., it becomes molten upon heating. The general chemistry of a metal includes at least one of the following properties: cation formation by losing electrons; basic or amphoteric oxides and hydroxides; low ionization energies and electron affinities; few outer shells electrons; electropositive; and, it is a reducing agent. Generally, the metals of Groups IA - VA, IB - VIIB, VIII, the lanthanides, and the actinides, thorium and

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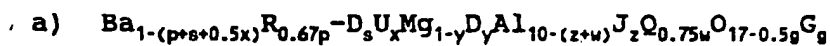
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uranium.

In addition, strain-free UCDP glasses can be produced. The number of different cation components and their concentrations in the end products can vary widely, as illustrated in the examples below. The purity, quality, homogeneity and yields of the end products are very high and precisely reproducible. Because of the intrinsic properties of the UCDP's products, they may be used in all refractory oxide syntheses, fabrication procedures and applications such as sensors, filters, wave-guides, electrooptics, photonics, high strength near-net-shape structures, superconductors, insulators, catalysts, films, fibers and nuclear waste management.

In a preferred aspect, the novel refractory oxides of this invention are produced from a metal oxyhalide precursor thereto selected from the group consisting of:



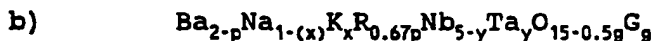
$D_s = Ca, Sr, Pb; G = F, Cl; Q = Si, Ge;$

$J = Cr, Ga, Ti, Mn, V, Fe, Co; U = Na, K;$

$D_y = Co, Cu, Ge, Ni, Zn; R = Y, \text{lanthanides};$

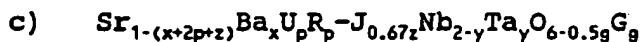
$0 \leq g \leq 33.7; 0 \leq p \leq 0.6; 0 \leq s \leq 1.0;$

$0 \leq x \leq 1.2; 0 \leq y \leq 1; 0 \leq z \leq 0.6; 0 \leq w \leq 7.5;$



$G = F, Cl; R = Y, \text{Lanthanides}$

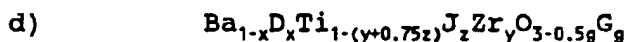
$0 \leq g \leq 29.7; 0 \leq p \leq 0.6; 0 \leq x \leq 1.0; 0 \leq y \leq 5.0;$



$G = F, Cl; U = Na, K;$

$J = Cr, Fe; R = Y, \text{Lanthanides};$

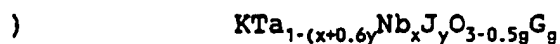
$0 \leq g \leq 11.7; 0 \leq p \leq 0.18; 0 \leq x \leq 1; 0 \leq y \leq 2; 0 \leq z \leq 0.18;$



$D = Sr, Pb, Ca;$

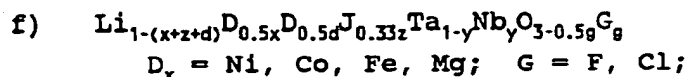
$G = F, Cl; J = Fe, Cr$

$0 \leq g \leq 5.7; 0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 0.1;$



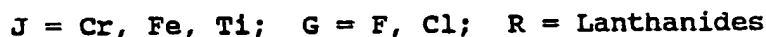
$G = F, Cl; J = Cr, Fe;$

$$0 \leq g \leq 5.7; \quad 0 \leq x \leq 1; \quad 0 \leq y \leq 0.1;$$



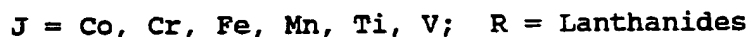
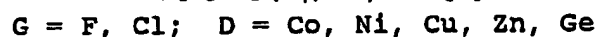
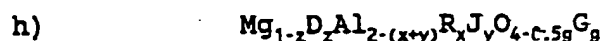
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$$0 \leq d \leq 0.12; \quad 0 \leq g \leq 5.7; \quad 0 \leq x \leq 1; \quad 0 \leq y \leq 1; \quad 0 \leq z \leq 0.4;$$

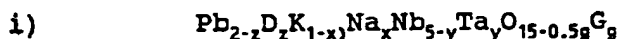


$$0 \leq g \leq 1.7; \quad 0 \leq x \leq 0.005; \quad 0 \leq y \leq 1; \quad 0 \leq z \leq 1;$$

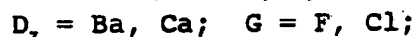
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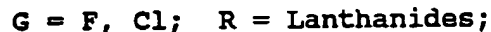
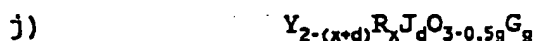
$$0 \leq g \leq 7.7; \quad 0 \leq x \leq 1; \quad 0 \leq y \leq 2; \quad 0 \leq z \leq 1;$$



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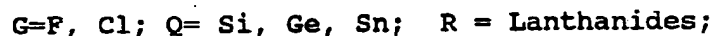
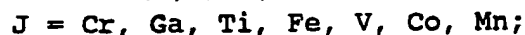


$$0 \leq g \leq 29.7; \quad 0 \leq x \leq 1, \quad 0 \leq y \leq 5, \quad 0 \leq z \leq 2;$$

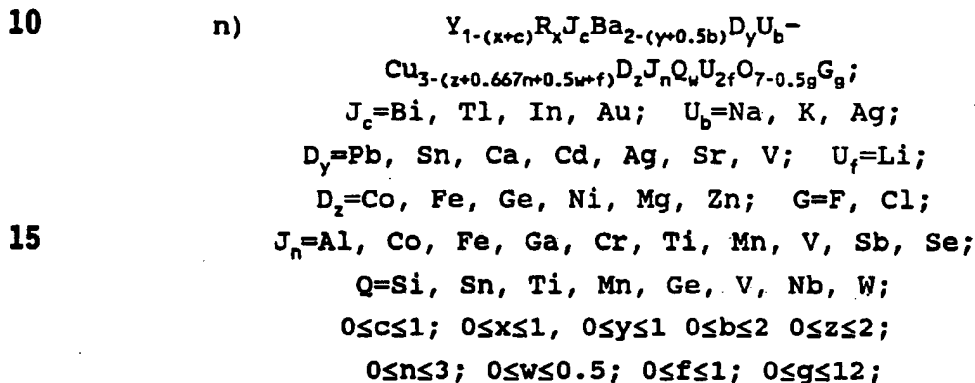
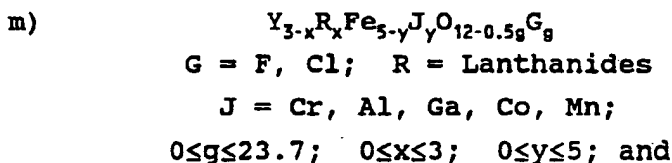
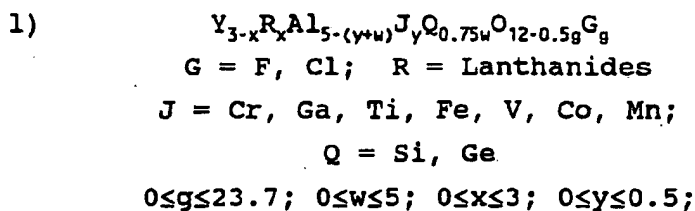


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$$0 \leq d \leq 0.15; \quad 0 \leq g \leq 5.7; \quad 0 \leq x \leq 2;$$



$$0 \leq g \leq 5.7; \quad 0 \leq x \leq 0.12; \quad 0 \leq y \leq 0.12; \quad 0 \leq w \leq 1.8;$$



where "U", "D", "R", "J", and "Q" are one or more: uni-  
 valent, divalent, rare-earth, trivalent and tetravalent  
 cations, respectively; and, "G" is one or more halogen  
 ions; and, each lower-case letter of the formulae denotes  
 a variable numerical value of the atomic ratio of that  
 chemical element in the composition.

The preferred refractory oxides of this invention  
 otherwise correspond to the above formulae without the  $G_g$   
 element.

In the context of this invention, the term hydrolysis  
 as used herein is the chemical reaction of a substance with  
 water or its ions. These ions, of course, are found in  
 both inorganic and organic classes of compounds. A cation  
 is either a positively charged ion or a metal ionically-  
 covalently bonded to a non-metal, e.g., Al bonded to  $O_2$  in  
 $Al_2O_3$ . The UCDP end products are transparent in the visible  
 region of the electromagnetic spectrum except, in some

cases, the end products which contain colored cations. The halides employed in this invention are halogen, e.g., F, Cl, Br and I, anions which are chemically bonded to more electropositive ions or radicals, e.g., metal ions (cations) or hydrogen ions.

5 A chemical complex composition of this invention consists of one or more metal halides bonded to oxygen, hydroxyl groups both. A metastable (labile) complex is a transitional state complex which may exhibit an overall  
10 excess electric charge(s). The refractory oxide products of this invention and their precursor complex compositions, can be manufactured as undoped, doped, solid solution, congruent melting or incongruent melting, stoichiometric or nonstoichiometric compositions. Precursors complex  
15 compositions are metal oxide compositions in which some of the oxygen anions are intentionally replaced by halogen anions, hydroxyl groups or a combination thereof; such as hydroxyhalide and oxyhalide complexes. Pure refractory oxide end products are essentially free of halogen anions and unintentional impurities.  
20

Crystallographic purity of a given compound can be determined by X-ray analysis and reported as a weight percent of an X-ray analyzed sample. Yield percent is the weight agreement between the actual and theoretical weights  
25 of the desired end product. X-ray purity and yield percents are given in the examples below. Each dispersed colloidal-like particle of UCDP compositions may consists of many molecules and/ions. When particle size diameters are less than about a hundred nanometers, the refractory  
30 oxide is called either a nanostructured or nanophased composition. These nanophased materials can be used to produce new classes of ceramics and ceramic composites which demonstrate enhanced magnetic, electronic and mechanical properties and can lead to advanced materials,  
35 engineering breakthroughs and new technologies.

Not only are the chemical and crystallographic characteristics of the refractory oxide end products excellent, the reproducible yields average ninety-three (93%) percent. Experimentation with reaction parameters can raise the yield even higher to that closely approaching theoretical. From small (laboratory scale) to very large (massive, commercial scale) quantities of high quality and purity refractory oxides can be produced by the UCDP. A commercial manufacturing level is preferred because of improved quality control, materials standardization, performance and lower costs. Small to massive quantity manufacture for a given refractory oxide can range from less than ten (10) grams per run to several tons or more per year.

In general, practicing the process involves the steps of calculating the amount of reactants required to produce the desired refractory oxide end product; weighing out and homogeneously mixing the reactants to form dispersed colloidal-like mixtures, which include reactant categories of at least one of: I) at least one halide whose cation forms the end product's cationic component and a sufficient volume of liquid water to ensure the thermal halide hydrolytic reactions will go to completion; II) at least one halide whose cation forms one of the end product's cationic components, a sufficient volume of liquid water to ensure the thermal halide hydrolytic reactions will go to completion and an oxide or a mixture of oxides whose cation or cations form the remainder of the reaction product's cation components; and III) at least one oxide whose cation forms the cationic component of the reaction product and an amount of a hydrogen halide composition sufficient to ensure the complete formation of the intermediate halide-oxide complexes.

The process procedure, involves the steps of heating a hydrated halide homogeneously dispersed colloidal-like reactant mixture or a hydrated halide-oxide homogeneously dispersed colloidal-like reactant mixture in an appropriate crucible and ordinarily in air and at ambient pressure to

a temperature at which a homogeneous solid state hydroxyhalide complex, containing only the cation or cations of the refractory oxide, is produced; it is then heated to its solid state hydroxyhalide metastable activated complex temperature where it decomposes over time to a solid state homogeneous oxyhalide complex; it is then heated to its solid state oxyhalide metastable activated complex temperature where it pyrolyzes over time to its novel refractory oxide end product; or, is heated to a still higher temperature where the solid state oxyhalide becomes a molten oxyhalide complex and over time pyrolyzes to its novel refractory oxide end product; or, the molten temperature is raised where the molten oxyhalide complex vaporizes and pyrolyzes over time to its novel refractory oxide end product. All of the refractory oxide end products are cationically homogeneous, transparent and of nanometer-scale particle size diameters.

The temperatures at which these various reactions occur in the process of this invention range from about ambient (20°C) temperature for the initial reaction to about 1700°C for the final refractory oxide production step and at virtually any pressure which does not adversely affect shifting chemical equilibria reactions. The length of time for a complex to sequentially decompose is principally a function of the complex composition, the quantity of the complex and the decomposition temperature employed. The reaction time periods are usually maintained for a plurality of hours at designated temperatures to ensure that a complete complex reaction is achieved. These reaction parameters can be empirically estimated and roughly *in situ* determined. More sophisticated known *in situ* thermo-analytical techniques can be used to determine the optimum UCDP reaction kinetic parameters, which can then be precisely reproduced.

The quantity of the reactant mixtures used in the examples below, ranged from three grams to seven grams. In commercial production, the runs can range from one or more kilograms. In general, the starting hydrated composition's

temperature is raised from ambient temperature to, e.g., up to about 150°C (Reaction I), and maintained at that temperature for a sufficient period of time, e.g., for about two hours or longer, to ensure the complete hydration of the reactant(s) and to dry the reaction product for further processing.

The hydroxyhalide complex reaction temperature is also maintained for a sufficient length of time, e.g., about four hours or longer, to ensure the complete conversion of the hydrated mixture to a solid state hydroxyhalide complex. The reaction temperature is then raised to its solid state hydroxyhalide metastable activated complex decomposition-temperature where, over time, e.g. for about four (4 hrs.) hours, the complex decomposes to a homogeneous solid state oxyhalide complex. The temperature is then raised to the oxyhalide's metastable activated complex decomposition-temperature where in about five (5 hr.) hours, the complex decomposes to its refractory oxide end product; or, the temperature is further raised to an oxyhalide complex molten decomposition-temperature where over an approximate five (5 hrs.) to eight (8 hrs.) hours, the molten phase complex decomposes to its refractory oxide end product; or, the oxyhalide complex molten temperature is again raised to a vapor phase decomposition-temperature where over an approximate five (5 hrs.) hours to eight (8 hrs.) hours, the vapor phase complex decomposes to its refractory oxide end product. All three refractory end products of the solid state, molten and vapor phases of the oxyhalide complex are of identical composition.

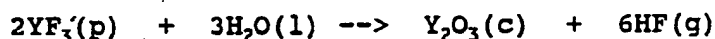
The specific decomposition-temperatures used depend upon the specific oxyhalide being pyrolytically decomposed but generally is about 100°C to 1500°C below the true melting point of the corresponding refractory oxide. Ordinarily and preferably the temperatures are maintained substantially constant, e.g., within about 5°C and preferably within about 1°C, during the UCDP. The generic process of this invention, therefore, provides a precise, highly reproducible yield process for manufacturing all



refractory oxide compositional categories at lower temperatures than heretofore feasible or possible and produces refractory oxide end products which are transparent, cationically homogeneous, with nanometer-scale particle sizes, of high quality and purity as verified by chemical and/or X-ray analyses. The invention also provides a method for the manufacture not only of refractory oxide compositions which are presently commercially available but also heretofore commercially unavailable known refractory oxides. The process also enables the manufacture of a potentially inexhaustible number of novel refractory compositions, including those disclosed herein.

In accordance with the process of this invention, doped refractory oxides, such as doubly doped (neodymium and chromium) yttrium aluminum garnet, titanium doped aluminum oxide, lithium tantalum niobate, yttrium oxyfluoride, yttrium barium copper oxide, and yttrium oxide can and have been produced. The doping can occur at any of the intermediate complex stages but conveniently occurs at the initial hydrolytic stage.

In general, UCDP compositions are manufactured by calculating the ratio of starting reagents (reactants) required to produce the selected refractory oxide (water in each instance being employed in excess of that theoretically required), mixing the reactants and implementing thermochemical reactions. For example, in the case of yttrium oxyfluoride (YOF) and yttrium oxide ( $Y_2O_3$ ), the overall reaction equation is:



The  $Y_2O_3$  free energy of formation @ 1823°K (1550°C), via UCDP, is ca. -192 Kcal mole<sup>-1</sup>. The theoretical hydrogen fluoride product weight loss percent is about 35%.

Reaction I:  $YF_3$  hydration (chemisorption ca. 20°C to ca. 150°C)

$2YF_3(p) + 3H_2O(l) \rightarrow 2[YF_3 \cdot 1.5H_2O](c) + \text{heat.}$

Reaction II: Thermochemical halide hydrolytic reactions and shifting chemical equilibria cause the

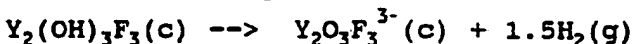
formation of a solid state hydroxyfluoride complex from ca. 150°C to ca. 500°C.



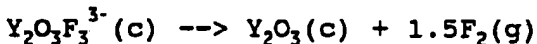
Reaction IIA: Oxide-hydrogen halide hydrolytic group alternate reaction to Reactions I & II.



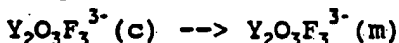
Reaction III: Increasing temperature (>500°C), shifting chemical equilibria and solid state activated hydroxyfluoride decomposition causes the formation of a solid state oxyfluoride complex at ca. 1000°C.



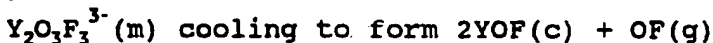
Reaction IIIA: Solid state activated oxyhalide complex decomposition to refractory end product at ca. 1100°C & 80 hrs.



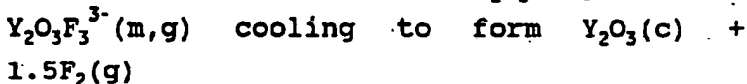
Reaction IV: The solid state activated oxyfluoride complex becomes molten at ca. 1125°C.



Reaction IVA: Translucent YOF crystallizes during either a five hour isothermal or programmed cooling period from ca. 1180°C to 1075°C.



Reaction IVB: Molten or vapor phase isothermal  $\text{Y}_2\text{O}_3\text{F}_3^{3-}(\text{m,g})$  decomposition temperature at ca. 1550°C or programmed cooling to 1250°C over eight hours produces transparent  $\text{Y}_2\text{O}_3$  crystals.



In the above equations, p=powder(anhyd.); l=liquid; g=gas; c=crystalline; m=molten; and --> = reaction direction and heat.

An implementation of the above UCDP manufacturing thermochemical reactions are as follows:

1. Write the appropriate chemical equations and calculate:

a) reactant molar ratios;

b) free energies at Reactions II-IVB temperatures; and

c) theoretical product weight loss percent for each reaction.

2. Use either ultrapur reactants or off-the-shelf chemical reactants which include: a) at least one halide and liquid water; or b) at least one oxide, at least one halide and liquid water; or, c) at least one hydrolyzable member of the group consisting of a metal oxide and a hydrogen halide composition or a combination thereof, calculate and weigh out each reactant and, sequentially, homogeneously dry-mix the reactants, slurry-mix to a homogeneously dispersed colloidal-like state, dry the uniform mixture up to about 150°C, and pulverize and sieve the mixture through a 200 mesh screen (Reaction I).
3. Place the powdered composition in a pre-weighed empty crucible, weigh and program heat the crucible to the appropriate temperature and hold for an appropriate time which ensures complete solid state hydroxyhalide complex formation (Reaction II).
4. Cool the furnace; weigh the crucible and determine the composition's wt% loss; pulverize the composition and sieve through 200 mesh screen. Use X-ray analysis to confirm the precursor complex phase has completely formed.
5. Compact and place the powdered composition in a pre-weighed empty crucible, weigh and program heat the crucible to a Reaction III temperature and maintain the contents at that temperature for a period of time sufficient to ensure the oxyhalide reaction has gone to completion. Determine wt % loss, pulverize, sieve and X-ray to confirm the presence of the precursor complex phase.
6. Compact the Step 5 composition and program heat it to a Reaction IIIA temperature. Maintain a constant (isothermal) temperature for a sufficient time period to ensure the desired decomposition of the solid state activated oxyhalide complex, which can be determined

by *in situ* weighing or *in situ* evaluating the volatile byproduct's pH.

7. Compact the Step 5 composition and program heat it to a Reaction IV temperature.
- 5 8. Obtain a precursor oxyhalide end product composition by performing a Reaction IVA procedure of: a) maintaining a constant (isothermal) temperature for a sufficient time period to ensure the desired decomposition of the activated complex, which can be determined by *in situ* weighing or *in situ* evaluating the volatile byproduct's pH; b) program cooling the molten temperature to a lower molten or solidification temperature; or, c) isothermally maintaining or program cooling an end product seed crystal in contact with the complex.
- 10 9. Heat the compacted composition from Step 7 to within a temperature range from about twenty (20°C) Celsius degrees to three hundred (300°C) Celsius degrees above the Reaction IV initial molten temperature.
- 15 10. Obtain a pure refractory oxide end product compound by performing the following Reaction IVB procedure of: a) isothermally maintaining the higher Step 9 temperature for a sufficient time period to ensure that the shifting chemical equilibria caused by the gas-forming reactions and the consuming decomposition reactions of the molten or vapor phase activated complexes to solid oxide are completed and the reaction phases are stabilized, which can be determined by *in situ* weighing or *in situ* evaluating the volatile byproduct's pH; b) program cooling the molten temperature to a lower molten or solidification temperature; or, c) isothermally maintaining or program cooling an end product seed crystal in contact with the molten complex.
- 20 11. Perform X-ray, chemical and infrared absorption analyses on the end product composition.
- 25 12. Anneal, if necessary to impart a specific property to the refractory oxide, in an appropriate gaseous
- 30
- 35

environment, such as dry or moist air, O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CO/CO<sub>2</sub>, HF, He or Ar at an annealing temperature and pressure.

The reactant categories are at least at least one of:

- 5 I) a metal halide and liquid water; II) an oxide, a metal halide and liquid water; and III) a metal oxide and a hydrogen halide composition whose cation is volatile, such as a hydrogen halide or an ammonium hydrogen halide. A reaction requirement is that at least either one metal  
10 halide is hydrolyzed or one metal hydroxyhalide complex is thermally decomposed to an end product refractory metal oxide. Reactions I & II correspond to reactant Categories I & II, respectively, while Reaction IIA correspond to Category III.

- 15 Category I reactants are used for Reaction I types of compositions. Category II reactants, in a very general way, are used to manufacture stoichiometric compositions which generally include both common-cation oxides or oxides different from the metal (cationic) halides. Identical  
20 oxide and halide cations reactants produce unary cation oxides whereas dissimilar cationic oxide and halide reactants produce binary and multi-component oxides. As the halides hydrolyze to hydroxyhalide complexes, the resulting gaseous hydrogen halide byproducts may react with  
25 additional oxide reactants to form additional complexes. For example, the hydrogen fluoride product gas [HF(g)] of Reaction II can be used to hydrolyze more oxide(s), e.g.,  
$$Y_2O_3(c) + 3HF(g) \longrightarrow Y_2(OH)_3F_3(c).$$
  
Reaction II equation thus reads:  $2[YF_3 \cdot 1.5H_2O](c) + Y_2O_3 \longrightarrow$   
30  $2Y_2(OH)_3F_3.$

- Category III reactants generally are used to: a) enhance precise reproducible dopant or solid solution product concentrations; b) combine with common cation halides which are unstable at elevated temperatures; i.e., sublime;  
35 c) enables the synthesis of precursor complexes for those cations which do not form stable elevated temperature halides; and, d) possibly maintain a given end product cationic oxidative state of a transition element. Also in

5 a very general way, Category III reactants are used to  
manufacture non-stoichiometric compositions. During  
hydrolysis, the metal-oxygen bonds of the Category III  
oxides may be less perturbed than comparable bonds of  
Category II oxides. Because quality non-stoichiometric  
10 compounds are difficult to produce, Reaction IIA (Category  
III reactants) is a more amenable environmental reaction  
for manufacturing higher quality non-stoichiometric  
compositions than Reaction II (Category II reactants).  
15 Byproduct furnace-exiting gases resulting from the  
reactions are ordinarily chemically neutralized.

The use of liquid water as a reactant as well as the  
use of excess liquid water is a substantial improvement  
over the prior art technique of using indeterminate moist  
15 gases or waters of crystallization as the hydrolysis water  
source reactant. The halides and oxides used in the UCDP  
are not only fully hydrated, which ensures complete hydro-  
lytic reactions, but also the liquid water, of appropriate  
pH, is a homogeneous reactant-mixing medium. The combined  
20 simultaneous chemical exothermic halide-hydration reaction  
and homogeneous physical slurry-mixing produces a homo-  
geneously dispersed colloidal-like reactant mixture from  
which all the UCDP precursor refractory oxide complexes are  
spawned.

25 When the final precursor oxyhalide complex decomposes,  
a novel structured refractory oxide is produced which is of  
uniform cation distribution, three dimensionally uniform  
and nanometer-scale particle sized. They are of high qual-  
ity and purity and obtained in high reproducible yield.  
30 They are ordinarily transparent and sometimes have one or  
more of electrostatic and magnetic properties. Thus, the  
optimum preparation of the homogeneously dispersed  
colloidal-like reactant mixture is largely responsible for  
the UCDP's capability to manufacture all refractory oxide  
35 compositional categories as well as for the favorable end  
product properties. Each oxide and metal halide reactant  
is individually prepared and hydrolyzed up through at least  
Reaction II, i.e., a hydroxyhalid complex of each reactant

is singularly produced. The hydroxyhalide complex reactants then can be combined and sequentially, homogeneously dry-mixed, slurry-mixed, dried, pulverized and further reacted. Using this process procedure ensures end product ultrahomogeneity, a product of the highest of purity and quality and reproducible yields approaching theoretical. The different hydrolytic reaction rates of each reactant's several complexes during the reactions appear to be of little criticality, particularly in light of the temperature magnitude of a Reaction IV final pyrolytic-temperature.

Although all halides may be used in the manufacture of refractory oxides by the UCPD, fluorides, chlorides and fluoride-chloride combinations are preferably used. Also additional reactants may be used, such as other halides, other oxides, hydroxides, carbonates, nitrates and sulfates; whether anhydrous or hydrated. Although ultrapure pure reactants may be used to produce refractory oxides of the highest of purity, off-the-shelf (reagent grade) chemical reactants generally are used because they become highly purified during the complex formation-decomposition reactions. Thus, the refractory end products of the UCPD can be manufactured very economically.

While the proposed reactions, which are assumed to be molecular complex reactions, are conceivably reversible, this invention is based on shifting chemical equilibrium reactions that proceed irreversibly to the right as the volatile components exit from the reaction vessel. A complete reaction has occurred when the products' theoretical and actual weights are equal.

Each example below exhibits a decomposition-temperature range derived from thermodynamic free energy calculations. The range is conveniently confirmed by heating a small (four gram) sample reactant mixture to each of the temperatures at which a chemical conversion occurs and maintaining the sample at each of those temperatures for at least about three hours. Microscopic examinations of the compositions can identify the molten phase ranges. A particular decomposition temperature is chosen because:

the composition's vapor pressure does not adversely affect the manufacturing process; of an estimated decomposition rate for that chosen temperature; and of a selected free energy value. While decomposition rates are directly influenced by temperature, shifting chemical equilibria are influenced by a free or controlled flow of volatile (gas) byproducts exiting from the furnace. The decomposition rates, therefore, may be rapid or slow as a function of both temperature and byproduct gas flow. Varying decomposition rates and temperature also appear to influence particle sizes.

While some activated complexes may solid-state decompose at temperatures from about 100°C to about 300°C below the molten Reaction IV decomposition-temperature, molten phase decompositions are preferred because of: 1) greater decomposition rates within a specified time period; 2) greater chemical complex purifications; and, 3) greater control over the nucleation and growth rates of crystalline compounds.

Except in special cases, when manufacturing pure ceramics, firings occur generally at ca. 550°C for 10 hours, ca. 1025°C for 5 hours and 1210°C for 12 hours before the final decomposition-temperature is reached. The compositions are powdered after each firing. In steps 3-10, reaction status can be evaluated from pH measurements of exiting furnace gases within an approximate 5.5 to 7.5 pH range and confirmed by *in situ* furnace-weighings and other thermoanalytical methods well known to those skilled in the art which may be used to determine reaction rate measurements. Compacting the later-stage complex compositions contribute to the UCDP's exactly reproducible end products.

In the UCDP's chemical vapor deposition procedure, chlorides are generally used rather than fluorides because chlorides melt at much lower temperatures and exhibit much higher vapor pressures at given temperature than fluorides.

To make a UCDP glass, a molten UCDP composition is quenched. Glass-c ramics are manufactured at elevated



temperatures by a two step glass transformation procedure of nucleation and crystal growth.

UCDP refractory oxide compositions are manufactured by one or more of the following pyrolytic procedures: a) program heating to a selected isothermal decomposition-temperature and maintaining the temperature for a pre-selected decomposition-time, i.e., solid state or molten phase pyrolyses; b) program heating beyond a given selected decomposition-temperature to a higher isothermal decomposition-temperature, i.e., increased pyrolytic rate or vapor phase pyrolysis; c) program cooling from a selected decomposition-temperature to a lower decomposition temperature, e.g., to retard grain size increase. Transparent, well formed and faceted single crystallites always appear to be present in crystalline batches irrespective of the pyrolytic procedure.

Process thermochemical reactions can be *in situ* monitored measured and controlled during the manufacturing procedure. Thus, the thermochemistry of each compositional system may be studied and reaction kinetics may be proposed and implemented. In addition, where an end product consists of more than one phase, the chemical composition of each phase may be determined and generally each phase can be individually UCDP manufactured.

In one aspect of the invention, a "reagent dispersion medium" can be used in the manufacture of refractory oxide end product, i.e., a medium of low melting reagents in which a precursor complex of the desired refractory oxide end product can be dissolved moltenly-dispersed and the low melting reagent dispersion medium can be converted to the same refractory oxide end product and collectively can provide the same cations in the same atomic ratio, particularly when using molten metal chlorides. Reagent dispersion media serve three functions, either separately or in combination thereof, as: 1) a homogeneous catalyst-like vehicle which increases the reaction rate by serving as: a) low viscosity homogeneous dispersion-like media at elevated transition temperatures by increasing the fre-

quency of colloidal-like particle (dispersed-like phase) collisions during the formations and decompositions of the complexes and the activated complex transitions to refractory oxides and volatile byproducts; 2) scavengers to remove extraneous ions from the starting precursor complex and thus from the resulting product produced therefrom; and, 3) natural convection dispersion-like media in the manufacture of large physical objects such as low density, near-net-shaped structures or solid high density single crystals.

The reagent dispersion medium can be present in the starting reaction mixture in a wide range of concentrations, e.g., from about one to about ninety-nine mole percent of the metal ion-containing reactant or reactants, provided it does not alter the metal cation profile of the reaction mixture.

An example of the use of a reagent dispersion medium which does not alter the cation composition of the reaction mixture in the manufacture of yttrium oxide is summarized as:

$$2.2\text{YF}_3(\text{p}) + 3\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Y}_2\text{O}_3(\text{c}) + 0.2\text{YF}_3(\text{c}) + 6\text{HF}(\text{g});$$
  
In the equation, the  $0.2\text{YF}_3(\text{c})$  acts as the reagent dispersion medium and constitutes about 11.4 wt.% of the sum of the two crystalline products. The residual reagent dispersion medium generally can be separated from desired end products by chemical dissolution.

A variety of furnaces and techniques can be used to manufacture refractory oxide compositions by the UCDP from solid, molten, or vapor phases. The furnace-pressure capabilities can range from negative pressures (vacuums) to overpressures greater than one atmosphere. Compacted reactant-mixture billets or platinum, ceramic or molybdenum crucibles can be used to hold the reacting compositions in the appropriate gas environments such as air, nitrogen, oxygen and hydrogen.

A mini-variational cationic concentration is the weight percent difference between the calculated theoretical weight percent and the chemically assayed

weight percent of an end product cation. For a given composition in the examples below, this difference is expressed as an overall cation accuracy equal to 100% minus the sum of the theoretically calculated and chemically assayed weight percent differences of all of the end product's cations, chemically analyzed as metals. On average, cationic accuracy measurements of the compositions, by wet chemical analyses, are equal to or greater than ninety-eight ( $\geq 98\%$ ) percent. In the examples below where the cation accuracy is high, no new X-ray lattice constants were determined for doped and solid solution compounds if a JCPD X-ray card does not exist. The lattice constants of these compounds are reported as the standard JCPD values for identical constituent compounds but of different concentrations.

Infrared absorption analyses have not detected any hydroxy-fluorides, oxyfluorides, fluorine, water or hydroxyl groups in the pure crystalline refractory oxide products of the UCDP.

Transparency at reduced temperatures is a property of most of the UCDP products and suggests nanometer-scale particle size diameters. However, some of them, such as the superconducting and magnetic oxides are colored and opaque due to their colored metal cation. Transparency and well-formed crystalline compositions may occur because as the homogeneously dispersed colloidal-like oxyhalide complexes thermochemically decompose uniformly, the consuming-complexes become electrically neutral, coagulate and become dense as they form refractory oxide end products. Both conventional and new complex transparent geometrically shaped articles can be produced by the UCDP. The potential applications for these geometrically-shaped objects include ceramic, automotive, electronic, and aerospace. *In situ* non-destructive evaluation (NDE) of these transparent objects can be made by visual or other optical techniques.

Crystalline transparent oxyhalide compounds may contribute significantly to materials science. They may substitute for pure oxide compounds in numerous materials

applications, such as laser element, magnetic, substrate, superconductor, non-linear and ceramic composite materials.

In crystalline compounds, grain sizes and densities can be varied as a function of composition, decomposition-temperature and time ranges, such that very small or large grains of partial or theoretical density can be manufactured. For example, transparent alpha  $\text{Al}_2\text{O}_3$  was solid-state

manufactured at  $1470^\circ\text{C}$  for ten (10) hours. In one batch, the average particle size was eighty-eight (88nm) nanometers in diameter and measured a density of  $3.987 \text{ gms./cm}^3$ .

The  $\text{Al}_2\text{O}_3$  was of very high crystallinity and essentially unagglomerated. In 1969, Cobb and Wallis, supra, suggested that this inventor's hydrolysis research produced unagglomerated (monodispersed) crystalline compositions.

UCDP manufactured nano-structured compositions exhibit either electrostatic or magnetic properties or both. For example, crystallites, up to  $1\frac{1}{2}$  mm on a side, adhere vigorously to metal forceps.

The thus-produced UCDP refractory oxides of this invention are useful for the same purposes as known refractory oxides. They are useful for all refractory oxide syntheses, fabrication procedures and applications such as sensors, filters, wave-guides, electrooptics, high strength near-net-shape structures, superconductors, insulators, catalysts, films, fibers and nuclear waste management because the intrinsic UCDP properties ensures uniform cationic distribution, strain-free structures, high purity, high quality and processed-controlled density materials at reduced temperatures. Additionally, because of the UCDP's generic ability to manufacture, reproducibly, virtually any refractory oxide composition of high quality, the UCDP is an extraordinary and powerful manufacturing process.

For example, if a three dimensional self-supporting structure is desired, the precursor metastable solid state activated oxyhalide complex can be compressed in the desired final shape or form d ther into with or without using a non-contaminating volatilizable or combustible

binder and the shaped product converted into the solid state of the corresponding refractory oxide article or a complex precursor in a fluid vehicle can be slip casted into a mold and the molded article then heated to the temperature at which the refractory oxide is produced; if discrete crystals of the refractory oxide desired, e.g., for use in lasers, the conversion of the complex can be conducted in the molten state; and if a ceramic coating on a substrate is desired the conversion of the complex can be conducted by vaporization thereof onto a substrate, e.g., a heated sheet, ribbon or wire, e.g., magnesium oxide, strontium titanate, titanium, silica, etc. Alternatively, such a coating can also be produced by dipping the substrate material in or passing it through a molten pool of the complex precursor.

Each example below is either a specific representative derivative compound of the parent compound or a specific parent compound selected for manufacture from the immediate below general formula group series. Each group is of similar chemical-type of compounds, within given concentration ranges and suggest similar Uniform Cation Distribution Process (UCDP) temperature-range manufacture. In general, a parent compound is one in which the elements' atomic ratios are integers (subscript numbers). In the examples below, air at atmospheric pressure, was the furnace gas environment and lanthanides are the atomic number elements 57 to 71 of the Chemical Periodic Table.

## GENERAL FORMULA GROUP SERIES

The novel refractory oxides described below are produced from a metal oxyhalide precursor, whose structure otherwise corresponds thereto except for the absence of the  $G_g$  element, selected from the group consisting of:

- 1.)  $Ba_{1-(2p+s+0.5x)}U_pR_pD_sAMg_{1-y}D_yAl_{10-(z+w)}J_zQ_{0.75w}O_{17-0.5g}G_g$ ,
- 2.)  $Ba_{2-2p}Na_{1-(x-p)}K_xR_pNb_{5-y}Ta_yO_{15-0.5g}G_g$ ,
- 3.)  $Sr_{1-(x+2p)}Ba_xU_pR_pJ_{0.67}Nb_{2-y}Ta_yO_{6-0.5g}G_g$ ,
- 4.)  $Ba_{1-x}D_xTi_{1-(y+0.75z)}J_zZr_yO_{3-0.5g}G_g$ ,
- 5.)  $KTa_{1-(x+0.6y)}Nb_xJ_yO_{3-0.5g}G_g$ ,
- 6.)  $Li_{1-(x+z+d)}D_{0.5x}D_{0.5d}J_{0.33z}Ta_{1-y}Nb_yO_{3-0.5g}G_g$ ,
- 7.)  $Mg_{1-(x+y+z)}D_zJ_{0.67}R_{0.67x}O_{1-0.5g}G_g$ ,
- 8.)  $Mg_{1-x}D_xAl_{2-y}J_yO_{4-0.5g}G_g$ ,
- 9.)  $Pb_{2-z}D_zK_{1-x}Na_xNb_{5-y}Ta_yO_{15-0.5g}G_g$ ,
- 10.)  $Y_{2-x}R_xJ_dO_{3-0.5g}G_g$ ,
- 11.)  $Al_{2-(x+y+w)}R_xJ_yQ_{0.75w}O_{3-0.5g}G_g$ ,
- 12.)  $Y_{3-x}R_xAl_{5(y+w)}J_yQ_{0.75w}O_{12-0.5g}G_g$ ,
- 13.)  $Y_{3-x}R_xFe_{5-y}J_yO_{12-0.5g}G_g$ ,
- 14.)  $Y_{1-(x+c)}J_cBa_{2-(y+0.5b)}D_yU_bCu_{(z+0.667n+0.5w+f)}D_zJ_nQ_wU_{2f}O_{7-0.5g}G_g$ ; where

"U", "D", "R", "J" and "Q" are one or more of: univalent, divalent, rare-earth, trivalent and tetravalent cations, respectively; and, "G" is one or more halogen ions. Lower case letters of the formulas represent variable atomic (cationic) ratio numerical values of the valence elements.

In addition to the specific refractory oxides of the examples hereinafter, other refractory oxide examples which can be produced by this process are:  $BaB_2O_4$ ,  $BaTiO_3$ ,  $Bi_2Sr_2CaCu_2O_8$ ,  $Bi_2Si_{1.5}O_6$ ,  $Li_{0.75}Mg_{0.13}NbO_3$ ,  $SrTiO_3$ ,  $ZnO$  and  $ZrO_2$ .

The technique to manufacture reproducibly end products of specific concentrations is to determine the cationic (atomic) percent concentration of each end product cation. Thus, each end product's cation concentration percent is the reactant's cation concentration percent which may be weighed as a pure halide, oxide, nitrate, hydroxide, sulfate, etc.

The UCDP manufacturing procedure, which illustrates Reactions I-IVB, as already set forth, is responsible for the production of an assortment of compositions. The below examples are given to exemplify the UCDP and the scope of the invention and are not intended to be limiting in the sense of the scope of the invention.

## EXAMPLE I

## General Formula



R=Y, lanthanides; D<sub>s</sub>=Ca, Sr, Pb; U=K, Na;

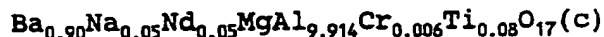
D<sub>y</sub>=Co, Cu, Ge, Ni, Zn; J=Cr, Ga, Ti, Mn, V, Fe, Co;

Q=Si, Ge;

0 ≤ p ≤ 0.6; 0.05 ≤ s ≤ 1; 0 ≤ w ≤ 7.5;

0 ≤ x ≤ 1.2; 0 ≤ y ≤ 1; 0 ≤ z ≤ 0.6

## Specific End Product Compound

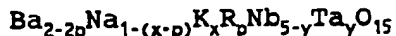


(New Composition)

The temperature of a three gram reactant mixture, consisting of in mole %, of 3.12BaF<sub>2</sub> + 0.02NaF + 0.02NdF<sub>3</sub> + 3.5MgF<sub>2</sub> + 20.6AlF<sub>3</sub> + 6.9Al<sub>2</sub>O<sub>3</sub> + 0.01Ti<sub>2</sub>O<sub>3</sub> + 58.5H<sub>2</sub>O, in an alumina crucible, was raised to the isothermal decomposition-temperature of 1370°C for five (5) hours. The temperature was then programmed cooled at 15°C per hour to 1175°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations were: Al=82.6 at.%, Mg=8.3 at.%, Ba=7.5 at.%, Ti=0.7 at%, Na=0.4 at.%, Nd=0.4 at.%, Cr=0.1 at.%. The cation accuracy is 99.1% and the X-ray purity is 99%. The crystallographic crystal class is hexagonal where a=5.625Å and c=22.62Å. The end product may be sieve-graded. After materials characterization, the compound is then ready for potential fabrications and applications, such as a solid state electrolyte, phosphor, red or tunable laser, and with the right dopants, an up-conversion blue-green laser.

## EXAMPLE II

## General Formula



R = Y, Lanthanides

0 ≤ p ≤ 0.4; 0 ≤ x ≤ 1; 0 ≤ y ≤ 5

## Specific End Product Compound



(New Composition)

5       The temperature of a three gram reactant mixture, consisting of in mole %, of 23.8BaF<sub>2</sub>, + 13.1NaF, + 0.63NdF<sub>3</sub>, + 20.3Nb<sub>2</sub>O<sub>5</sub> + 10.9Ta<sub>2</sub>O<sub>5</sub> + 31.5H<sub>2</sub>O, in an alumina crucible, was raised to the isothermal decomposition-temperature of

10       1250°C for five (5) hours. The temperature was then programmed cooled at 20°C per hour to 1160°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations were: Ba=23.7 at.%, Na=13.1 at.%, Nd=0.6 at.%, Nb=40.8 at.% and Ta=21.8 at.%. The cation accuracy is

15       98.4% and the X-ray purity is 100%. The crystal structure is tetragonal with a=12.473Å and c=3.940Å. The compound may be sieve-graded. After materials characterization, the compound is then ready for potential fabrication and application, such as a dual-role nonlinear dielectric and self-frequency doubling laser.

      In the same way, the refractory oxide Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub> is produced from 25 mole% BaF<sub>2</sub> + 12.5 mole% NaF + 31.3 mole% Nb<sub>2</sub>O<sub>5</sub> + 31.3 mole% H<sub>2</sub>O.



## EXAMPLE III

## General Formula



J = Cr, Fe; U = Na, K; R = Y, Lanthanides

5  $0 \leq p \leq 0.18$ ;  $0 \leq x \leq 1$ ;  $0 \leq y \leq 2$ ;  $0 \leq z \leq 0.18$

## Specific End Product Compound



10 The temperature of a three gram reactant mixture, consisting of in mole % of  $20.0\text{SrF}_2 + 13.3\text{BaF}_2 + 33.3\text{Nb}_2\text{O}_5 + 33.3\text{H}_2\text{O}$ , in a platinum crucible, was raised to the isothermal decomposition-temperature of  $1300^\circ\text{C}$  for five (5) hours. The temperature was then programmed cooled at  $30^\circ\text{C}$  per hour to  $1150^\circ\text{C}$  and the furnace ambiently cooled to room temperature. The cation reactant concentrations were: Sr=20.0 at.%, Ba=13.3 at.% and Nb=66.7 at. % The cation accuracy is 99.7% and the X-ray purity is 100%. The crystal structure is tetragonal with  $a=12.451\text{\AA}$  and  $c=3.931\text{\AA}$ . The product is suitable for use in electro-optical fabrications and applications.

20

## EXAMPLE IV

## General Formula



J = Cr, Fe;

$0 \leq x \leq 1$ ;  $0 \leq y \leq 0.1$

25

## Specific End Product Compound



30 The temperature of a three gram reactant mixture, consisting of in mole%,  $50\text{KF} + 15.7\text{Ta}_2\text{O}_5 + 9.3\text{Nb}_2\text{O}_5 + 25\text{H}_2\text{O}$ , in an alumina crucible, was raised to the isothermal decomposition-temperature of  $1055^\circ\text{C}$  for five (5) hours. The temperature was then programmed cooled at  $15^\circ\text{C}$  per hour to  $990^\circ\text{C}$  and the furnace ambiently cooled to room temperature. The cation reactant concentrations were: K=50. at.%, Ta=31.5 at.% and Nb=18.5 at.%. X-ray purity is 90%. The crystal structure is tetragonal with  $a=12.5847\text{\AA}$  and  $c=3.9811\text{\AA}$ . The compound may be sieve-graded. By adjustment of reaction conditions to increase X-ray purity to 98% or

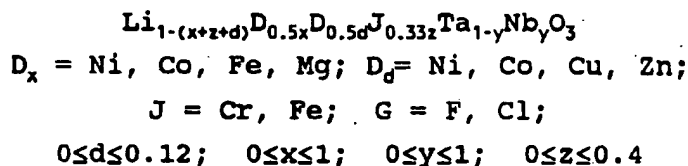
35

higher, the product is suitable for use in electro-optical fabrications and applications.

#### EXAMPLE V

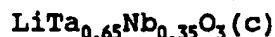
##### General Formula

5



##### Specific End Product Compound

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The temperature of a three gram reactant mixture, consisting of in mole%, 50LiF + 8.8Nb<sub>2</sub>O<sub>5</sub> + 16.3Ta<sub>2</sub>O<sub>5</sub> + 25H<sub>2</sub>O, in an alumina crucible, was raised to the isothermal decomposition-temperature of 1160°C for five (5) hours. The temperature was then programmed cooled at 20°C per hour to 1000°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations were:

15

Li=50.0 at.%, Ta=32.5 at.% and Nb=17.5 at.%.

The cation accuracy is 99.5% and the X-ray purity is 100%.

20

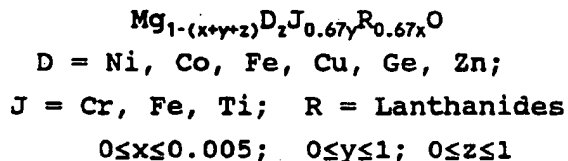
The crystal structure is rhombohedral with  $a=5.1539\text{\AA}$  and  $c=13.81512\text{\AA}$ . The compound may be sieve-graded. After materials characterization, the compound is then ready for potential electro-mechanical transduction fabrications and applications.

25

#### EXAMPLE VI

##### General Formula

30



##### Specific End Product Compound



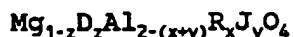
The temperature of a three gram reactant mixture, consisting of in mole %, 50MgF<sub>2</sub> + 50H<sub>2</sub>O, in a magnesium oxide crucible, was raised to the isothermal decomposition-temperature of 1290°C for eight (8) hours. The temperature

35

was then programmed cooled at 20°C per hour to 1050°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations was: Mg=100 at.%. The cation accuracy is 99.5% and the X-ray purity is 100%. The crystal class is cubic with  $a=4.213\text{\AA}$ . The compound may be sieve-graded. The product is suitable for use in infrared transmission and substrate fabrications and applications.

#### EXAMPLE VII

##### General Formula

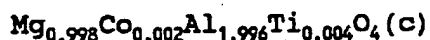


D = Co, Ni, Cu, Zn, Ge

J = Co, Cr, Fe, Mn, Ti, V; R = Lanthanides

$0 \leq x \leq 1$ ;  $0 \leq y \leq 2$ ;  $0 \leq z \leq 1$

##### Specific End Product Compound

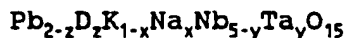


(New Composition)

The temperature of a three gram reactant mixture, consisting of in mole%, of 33.2MgF<sub>2</sub> + 0.07CoO + 0.05Ti<sub>2</sub>O<sub>3</sub> + 39.8AlF<sub>3</sub> + 13.3Al<sub>2</sub>O<sub>3</sub> + 33.4H<sub>2</sub>O, in an alumina crucible, was raised to the isothermal decomposition-temperature of 1450°C for ten (10) hours. The temperature was then programmed cooled at 25°C per hour to 1150°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations were: Mg=33.27 at.%, Co=0.07 at.%, Al=66.53 at.%, Ti=0.13 at.%. The cation accuracy is under analysis and the X-ray purity is 90%. The crystal class is cubic with  $a=8.0828\text{\AA}$ . The compound may be sieve-graded. By adjustment of reaction conditions the X-ray purity can be increased for use in ultra-violet light filter, phosphor and laser fabrications and applications.

## EXAMPLE VIII

## General Formula



$$0 \leq x \leq 1; \quad 0 \leq y \leq 5; \quad 0 \leq z \leq 2$$

## Specific End Product Compound



The temperature of a three gram reactant mixture, consisting of in mole%,  $25\text{PbF}_2 + 12.5\text{KF} + 31.3\text{Nb}_2\text{O}_5 + 31.3\text{H}_2\text{O}$ , in an alumina crucible, was raised to the isothermal decomposition-temperature of  $1120^\circ\text{C}$  for five (5) hours. The temperature was then programmed cooled at  $10^\circ\text{C}$  per hour to  $1070^\circ\text{C}$  and the furnace ambiently cooled to room temperature. The cation reactant concentrations were:

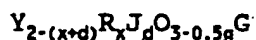
$$\text{Pb}=25.0 \text{ at.}\%, \text{ K}=12.5 \text{ at.}\%, \text{ Nb}=62.5 \text{ at.}\%.$$

The cation accuracy is 99.9% and the X-ray purity is 100%. The crystal class is orthorhombic with  $a=17.757\text{\AA}$ ,  $b=18.011\text{\AA}$ ,  $c=3.917\text{\AA}$ . The compound may be sieve-graded. The product can be used in ferroelectric-ferroelastic fabrications and applications.

## EXAMPLE IX

The following illustrates the preparation of the oxyhalides of this invention.

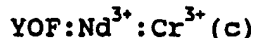
## General Formula



$\text{R} = \text{Lanthanides}; \text{G} = \text{F}, \text{Cl}; \text{J} = \text{Cr}, \text{Ga}, \text{Ti}, \text{Fe}, \text{Al}, \text{V}, \text{Co}, \text{Mn};$

$$0 \leq d \leq 0.4; \quad 0 \leq g \leq 5.7; \quad 0 \leq x \leq 2$$

## Specific End Product Compound



wherein  $\text{YF}_3(\text{c})$ ,  $\text{Nd}^{3+}$  &  $\text{Cr}^{3+} = 10^{20.2}$  &  $10^{18.1}$  Ions  $\text{cm}^{-3}$ .

The temperature of a three gram reactant mixture, consisting of in mole%,  $50\text{YF}_3 + 50\text{H}_2\text{O}$ , in an alumina crucible, was raised to the isothermal decomposition-temperature of  $1200^\circ\text{C}$  for six (6) hours. The temperature was then programmed cooled at  $10^\circ\text{C}$  per hour to  $1088^\circ\text{C}$  and the furnace ambiently cooled to room temperature. The product concen-

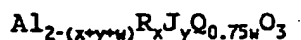
trations are: Y=32.856 at.%, O=33.330 at.%, F=33.330 at.%,  
Nd=0.480 at.%, Cr=0.004 at.%. The cation accuracy is 100 %  
and the X-ray purity is 60%. cubic ( $a=5.374\text{\AA}$ ) and 40%  
tetragonal ( $a=3.918\text{\AA}$ ,  $c=5.442\text{\AA}$ ). The compound may be  
5 sieve-graded. The product is suitable for use in doubly  
doped laser element applications.

The same product is produced from 33 mole %  $\text{YF}_3$  +  
17mole %  $\text{Y}_2\text{O}_3$  + 50 mole%  $\text{H}_2\text{O}$ .

#### EXAMPLE X

10

##### General Formula



Q = Si, Ge, Sn;

R = Lanthanides; J = Cr, Ga, Ti, Fe, V, Co, Mn;

$0 \leq x \leq 1$ ;  $0 \leq y \leq 0.12$ ;  $0 \leq w \leq 1.8$ ;

15

##### Specific End Product Compound



20

The temperature of a three gram reactant mixture, con-  
sisting of in mole%,  $12\text{AlF}_3 + 4\text{Al}_2\text{O}_3 + 20\text{NdF}_3 + 60\text{H}_2\text{O}$ , in an  
alumina crucible, was raised to the isothermal decomposi-  
tion-temperature of  $1430^\circ\text{C}$  for six (6) hours. The tempe-  
rature was then programmed cooled at  $15^\circ\text{C}$  per hour to  
1150°C and the furnace ambiently cooled to room  
temperature. The cation reactant concentrations were:  
Al=50.0 at.%, Nd=50.0 at.%. The cation accuracy is 100%  
25 and the X-ray purity is 90%. The crystal class is rhombo-  
hedral with  $a=5.3211\text{\AA}$  and  $c=12.9174\text{\AA}$ . After materials  
characterization, the compound may be sieve-graded. By  
adjustment of reaction conditions, X-ray purity can be  
increased to 98% or higher. The product is suitable for use  
30 in infrared window and substrate fabrications and  
applications.

35

In the same way, the same reaction product is produced  
by reacting 20 mole%  $\text{AlF}_3$  + 20 mole%  $\text{NdF}_3$  + 60mole%  $\text{H}_2\text{O}$  and  
transparent alumina is produced by reacting 57 mole%  
 $\text{AlF}_3 \cdot 3\text{H}_2\text{O} + 43$  mole%  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_{1.998}\text{Cr}_{0.002}\text{O}_3$  is produced from 24  
mole%  $\text{AlF}_3$  + 7.9 mole%  $\text{Al}_2\text{O}_3$  + 0.05 mol%  $\text{Cr}_2\text{O}_3$  and 60 mole %  
 $\text{H}_2\text{O}$ ,  $\text{Al}_{1.995}\text{Ti}_{0.005}\text{O}_3$  is produced from 75 mole%  $\text{AlF}_3 \cdot 3\text{H}_2\text{O} + 24.67$

mole%  $\text{Al}_2\text{O}_3$  + 0.15 mol %  $\text{Ti}_2\text{O}_3$  and  $\text{Al}_{1.988}\text{Nd}_{0.01}\text{Cr}_{0.002}\text{O}_3$  is produced from 35.9 mole%  $\text{AlF}_3$  + 0.28 mole%  $\text{NdF}_3$  + 0.03 mole%  $\text{Cr}_2\text{O}_3$  + 54.2 mole%  $\text{H}_2\text{O}$ .

# EXAMPLE XI

## General Formula

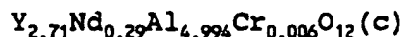


J = Cr, Ga, Ti, Fe, V, Co, Mn;

Q = Si, Ge; R = Lanthanides

$0 \leq x \leq 3$ ;  $0 \leq y \leq 0.5$ ;  $0 \leq w \leq 5$ ;

## Specific End Product Compound



The temperature of a three gram reactant mixture, consisting of in mole% of,  $13.6\text{YF}_3$  +  $1.5\text{NdF}_3$  +  $14.9\text{AlF}_3$  +  $5\text{Al}_2\text{O}_3$  +  $60\text{H}_2\text{O}$  +  $150\text{ppmCr}_2\text{O}_3$ , in an alumina crucible, was raised to the isothermal decomposition-temperature of  $1430^\circ\text{C}$  for six (6) hours. The temperature was then programmed cooled at  $15^\circ\text{C}$  per hour to  $1150^\circ\text{C}$  and the furnace ambiently cooled to room temperature. The cation reactant concentrations were:

Y=33.87 at.%, Nd=3.63 at.%, Al=62.42 at.%, Cr=0.08 at.%.

The cation accuracy is 99% and the X-ray purity is 99%. The crystal class is cubic where  $a=12.009\text{\AA}$ . The compound may be sieve-graded. The product is suitable for use in doubly doped laser fabrications and applications.

In the same way, the same product is produced from  $2.71\text{YF}_3$  +  $0.29\text{NdF}_3$  +  $4.99\text{AlF}_3$  +  $0.003\text{Cr}_2\text{O}_3$  +  $12\text{H}_2\text{O}$ .

## EXAMPLE XII

## General Formula



J = Cr, Al, Ga, Co; R = Lanthanides

5  $0 \leq x \leq 3; 0 \leq y \leq 2.5;$

## Specific End Product Compound



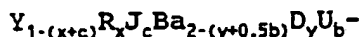
10 The temperature of a three gram reactant mixture, consisting of in a platinum crucible, was raised to the isothermal decomposition-temperature of 1350°C for ten (10) hours. The temperature was then programmed cooled at 15°C per hour to 1100°C and the furnace ambiently cooled to room temperature. The cation reactant concentrations were:

Y=37.5 at.%, Fe=62.5 at.%.

15 The cation accuracy is 100% and the X-ray purity is 90%. The crystal class is cubic where  $a=12.3788\text{\AA}$ . The compound may be sieve-graded. By adjustment of reaction conditions, X-ray purity is increased to 98% or higher. The product is suitable for use in magnetic device fabrications and  
20 applications.

## EXAMPLE XIII

## General Formula



25  $J_c=Bi, Tl, In, Au; U_b=Na, K, Ag;$

$D_y=Pb, Sn, Ca, Cd, Ag, Sr, V; D_z=Co, Fe, Ge, Ni, Mg, Zn;$

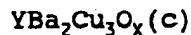
$J_n=Al, Co, Fe, Ga, Cr, Ti, Mn, V, Sb, Se; U_f=Li;$

$Q=Si, Sn, Ti, Mn, Ge, V, Nb, W;$

$0 \leq c \leq 1; 0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq b \leq 2; 0 \leq z \leq 2;$

30  $0 \leq n \leq 3; 0 \leq w \leq 0.5; 0 \leq f \leq 1;$

## Specific End Product Compound



YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> and derivative YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> compositions were UCDP  
35 manufactured with and without using 15 wt.% reagent dispersion medium [YF<sub>3</sub>=1.9 mole%, BaCl<sub>2</sub>=10.31 mole%, CuCl<sub>2</sub>=37.36 mole%, H<sub>2</sub>O=50.45 mole%]. The compositions manufactured were:

- 1)  $\text{YBa}_2\text{Cu}_3\text{O}_x$  - 6.3gms. reactant
- 2)  $[\text{YBa}_2\text{Cu}_3\text{O}_x]_{0.85} + [\text{YBa}_{5.48}\text{Cu}_{19.85}\text{O}_x]_{0.15}$  - 7.7gms. reactant
- 3)  $\text{YBa}_{6.922}\text{Cu}_{19.215}\text{O}_x$  - 3.3gms. reactant
- 4)  $[\text{YBa}_{6.922}\text{Cu}_{19.215}\text{O}_x]_{0.85} + [\text{YBa}_{5.48}\text{Cu}_{19.85}\text{O}_x]_{0.15}$

5

3.8gms. reactant.

The reactant's mole percents were:

Sample #1:  $\text{YF}_3=10.4$ ;  $\text{BaF}_2=21.4$ ;  $\text{CuO}=31.4$ ;  $\text{H}_2\text{O}=36.8$

Sample #2: Sample #1 (85 wt.%) + [ $\text{YCl}_3=1.9$ ;  $\text{BaCl}_2=10.31$ ;  $\text{CuCl}_2=37.36$ ;  $\text{H}_2\text{O}=50.45$ ] (15 wt.%).

10

Sample #3:  $\text{YF}_3=1.05$ ;  $\text{Y}_2\text{O}_3=1.05$ ;  $\text{BaF}_2=6.38$ ;  $\text{BaO}=12.75$ ;  $\text{CuO}=70.81$ ;  $\text{H}_2\text{O}=7.96$ .

Sample #4: Sample #3 (85 wt.%) + [ $\text{YCl}_3=1.9$ ;  $\text{BaCl}_2=10.31$ ;  $\text{CuCl}_2=37.36$ ;  $\text{H}_2\text{O}=50.45$ ] (0.15% wt%)

15

The four reactant compositions, in alumina crucibles, were simultaneously heat treated at  $995^\circ\text{C}$  for thirty (30) hours. The reagent dispersion medium's melting point is about  $280^\circ\text{C}$  and its end product formula is  $\text{YBa}_{5.48}\text{Cu}_{19.85}\text{O}_x$ . Because of the reagent dispersion medium's low melting point, it serves well as a dispersion-like medium, as earlier discussed. While all four samples demonstrate the UCDP approach leads to high reproducible superconductor yields, sample #4 material is a combination of numerous single crystallites and polycrystalline aggregates. This technique thus enables the UCDP manufacture of a number of different physical forms including fibers.

25

30

From a different and singular batch run of  $995^\circ\text{C}$  for twelve hours, Sample #1 crystallites were produced from solid state and vapor phase manufacture. Numerous black thin platelets, which are superconductors, measure two millimeters (2 mm) long by one and a half millimeters ( $1\frac{1}{2}$  mm) wide. Also from the same batch, many stand-alone equi-three-dimensional, highly light-reflective, shiny black crystallites which measure about 0.6 millimeters on a side and appear to be single crystals, were also observed as well as aggregates of three-dimensional crystallites.

35

While the thermochemical halide hydrolytic formation and decomposition of activated chemical complexes of the invention have been described by reference to preferred



embodiments in the foregoing examples, it is to be understood that the claims define the embodiments thereof which fall within the scope and spirit of the invention.

**WHAT IS CLAIMED IS:**

1. A process capable of producing in large commercial scale amounts a substantially pure refractory oxide which has an homogeneous cation distribution and a particle size diameter of less than 100 nanometers, which comprises producing and isolating a substantially pure cationically homogeneous metal oxyhalide which is pyrolytically convertible by heat alone to the refractory oxide and then heating the isolated metal oxyhalide, in a reaction medium having a metal cation composition stoichiometrically identical to that of the refractory oxide, to a temperature at which the metal oxyhalide is converted pyrolytically to the corresponding homogeneous refractory oxide.

2. The process of claim 1, wherein the substantially pure cationically homogeneous metal oxyhalide is produced by the steps of (a) mixing with liquid water at least one metal halide, alone or in mixture with a metal oxide, which halide and oxide are convertible to a refractory oxide, or by mixing a refractory oxide with an aqueous hydrogen halide composition, to produce a homogeneous colloidal-like fully hydrated halide-oxide reactant mixture; and (b) heating the thus-produced hydrated halide-oxide reactant mixture to a temperature at which the refractory oxide end product is produced, optionally with isolation of one or both of the intermediately produced solid state hydroxyhalide complex and oxyhalide complex.

3. A process according to claim 1, wherein the starting reactants comprise liquid water and at least one metal fluoride or metal chloride or both.

4. A process according to claim 1, wherein the starting reactants comprise liquid water, at least one metal oxide and at least one metal fluoride or metal chloride or both.

5. A process according to claim 1, wherein the starting reactants comprise at least one metal oxide and one or both of an aqueous hydrogen fluoride composition and an aqueous hydrogen chloride composition.

6. A process according to claim 1, wherein the temperature at which a reaction occurs is maintained substantially constant for a plurality of hours before the intermediate complex is heated to a higher reaction temperature.

7. A process according to claim 1, wherein the refractory oxide is formed in the presence of reagent dispersion medium.

8. A process according to claim 1, wherein the starting reactants are 71 mole%  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  + 29 mole%  $\text{Al}_2\text{O}_3$  and the refractory oxide is  $\text{Al}_2\text{O}_3$ .

9. A process according to claim 1, wherein the starting reactants are 12 mole%  $\text{AlF}_3$  + 8 mole%  $\text{Al}_2\text{O}_3$  + 20 mole%  $\text{NdF}_3$  + 60 mole%  $\text{H}_2\text{O}$  and the refractory oxide is  $\text{AlNdO}_3$ .

10. A process according to claim 1, wherein the starting reactants are 25 mol%  $\text{BaF}_2$  + 12.5 mole%  $\text{NaF}$  + 31.3mole%  $\text{Nb}_2\text{O}_5$  + 31.3 mole%  $\text{H}_2\text{O}$  and the refractory oxide is  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ .

11. A process according to claim 1, wherein the starting reactants are 23.8 mole%  $\text{BaF}_2$  + 13.1 mole%  $\text{NaF}$  + 0.6 mole%  $\text{NdF}_3$  + 20.4 mole%  $\text{Nb}_2\text{O}_5$  + 10.9 mole%  $\text{Ta}_2\text{O}_5$  + 31.3 mole%  $\text{H}_2\text{O}$  and the refractory oxide is  $\text{Ba}_{1.9}\text{Na}_{1.05}\text{Nd}_{0.05}\text{Nb}_{3.26}\text{Ta}_{1.74}\text{O}_{15}$ .

12. A process according to claim 1, wherein the starting reactants are 28.6 mole% KF + 9.0 mole% Ta<sub>2</sub>O<sub>5</sub> + 5.3 mole% Nb<sub>2</sub>O<sub>5</sub> + 42.9 mole% HF + 14.3 mole% H<sub>2</sub>O and the refractory oxide is KTa<sub>0.63</sub>Nb<sub>0.37</sub>O<sub>3</sub>.

13. A process according to claim 1, wherein the starting reactants are 29.8 mole% YF<sub>3</sub> + 6.4 mole% Y<sub>2</sub>O<sub>3</sub> + 63.8 mole% H<sub>2</sub>O and the refractory oxide is Y<sub>2</sub>O<sub>3</sub>.

14. A process according to claim 1, wherein the starting reactants are 16 mole% YF<sub>3</sub> + 1.7 mole% NdF<sub>3</sub> + 20.6 mole% AlF<sub>3</sub> + 0.02 mole% Cr<sub>2</sub>O<sub>3</sub> + 57.4 mole% H<sub>2</sub>O and the refractory oxide is Y<sub>2.71</sub>Nd<sub>0.29</sub>Al<sub>4.99</sub>Cr<sub>0.006</sub>O<sub>12</sub>.

15. A process according to claim 1, wherein the starting reactants and dispersion medium are, respectively, 85 wt.% of [1.1 mole% YF<sub>3</sub> + 1.1 mole% Y<sub>2</sub>O<sub>3</sub> + 6.4 mole% BaF<sub>2</sub> + 12.8 mole% BaO + 70.8 mole% CuO + 8 mole% H<sub>2</sub>O] + 15 wt% of [1.9 mole% YCl<sub>3</sub> + 10.3 mole% BaCl<sub>2</sub> + 37.4 mole% CuCl<sub>2</sub> + 50.5 mole% H<sub>2</sub>O] and the refractory oxide is [YBa<sub>6.92</sub>Cu<sub>19.2</sub>O<sub>x</sub>]<sub>0.85</sub> + reagent dispersion medium [YBa<sub>5.5</sub>Cu<sub>19.9</sub>O<sub>x</sub>]<sub>0.15</sub>

16. An inorganic metal oxide selected from the group consisting of substantially pure cationically homogeneous refractory oxides having a nanometer particle size diameter distribution of from about 1 to 100 nm and three dimensional crystallinity.

17. An inorganic metal oxide according to claim 16 selected from the group consisting of:

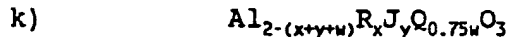
- a)  $Ba_{1-(p+s+0.5x)}R_{0.67p}D_sU_xMg_{1-y}D_yAl_{10-(z+w)}J_zQ_{0.75w}O_{17}$   
 $D_s = Ca, Sr, Pb; G = F, Cl; Q = Si, Ge;$   
 $J = Cr, Ga, Ti, Mn, V, Fe, Co; U = Na, K;$   
 $D_y = Co, Cu, Ge, Ni, Zn; R = Y, \text{lanthanides};$   
 $0 \leq p \leq 0.6; 0 \leq s \leq 1.0;$   
 $0 \leq x \leq 1.2; 0 \leq y \leq 1; 0 \leq z \leq 0.6; 0 \leq w \leq 7.5;$
- b)  $Ba_{2-p}Na_{1-(x)}K_xR_{0.67p}Nb_{5-y}Ta_yO_{15}$   
 $0 \leq p \leq 0.6; 0 \leq x \leq 1.0; 0 \leq y \leq 5.0;$
- c)  $Sr_{1-(x+2p+z)}Ba_xU_pR_pJ_{0.67z}Nb_{2-y}Ta_yO_6;$   
 $U = Na, K;$   
 $J = Cr, Fe; R = Y, \text{Lanthanides};$   
 $0 \leq p \leq 0.18; 0 \leq x \leq 1; 0 \leq y \leq 2; 0 \leq z \leq 0.18;$
- d)  $Ba_{1-x}D_xTi_{1-(y+0.75z)}J_zZr_yO_3$   
 $D = Sr, Pb, Ca;$   
 $J = Fe, Cr$   
 $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 0.1;$
- e)  $KTa_{1-(x+0.6y)}Nb_xJ_yO_3$   
 $J = Cr, Fe;$   
 $0 \leq x \leq 1; 0 \leq y \leq 0.1;$
- f)  $Li_{1-(x+z+d)}D_{0.5x}D_{0.5d}J_{0.33z}Ta_{1-y}Nb_yO_3$   
 $D_x = Ni, Co, Fe, Mg;$   
 $D_d = Ni, Co, Cu, Zn; J = Cr, Fe; G = F, Cl$   
 $0 \leq d \leq 0.12; 0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 0.4;$
- g)  $Mg_{1-(x+y+z)}D_zJ_{0.67y}R_{0.67x}O_{10}$   
 $D = Ni, Co, Fe, Cu, Ge, Zn;$   
 $J = Cr, Fe, Ti; R = \text{Lanthanides}$   
 $0 \leq g \leq 1.7; 0 \leq x \leq 0.005; 0 \leq y \leq 1; 0 \leq z \leq 1;$
- h)  $Mg_{1-z}D_zAl_{2-(x+y)}R_xJ_yO_4$   
 $D = Co, Ni, Cu, Zn, Ge$   
 $J = Co, Cr, Fe, Mn, Ti, V; R = \text{Lanthanides}$   
 $0 \leq x \leq 1; 0 \leq y \leq 2; 0 \leq z \leq 1;$
- i)  $Pb_{2-z}D_zK_{1-x}Na_xNb_{5-y}Ta_yO_{15}$   
 $D_z = Ba, Ca;$   
 $0 \leq x \leq 1, 0 \leq y \leq 5, 0 \leq z \leq 2;$



R = Lanthanides;

J = Cr, Ga, Ti, Fe, Al, V, Co, Ni, Cu, Mn;

$0 \leq d \leq 0.15$ ;  $0 \leq g \leq 5.7$ ;  $0 \leq x \leq 2$ ;



J = Cr, Ga, Ti, Fe, V, Co, Mn;

Q = Si, Ge, Sn; R = Lanthanides;

$0 \leq x \leq 0.12$ ;  $0 \leq y \leq 0.12$ ;  $0 \leq w \leq 1.8$ ;



R = Lanthanides

J = Cr, Ga, Ti, Fe, V, Co, Mn;

Q = Si, Ge

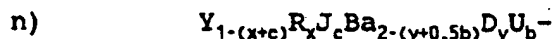
$0 \leq w \leq 5$ ;  $0 \leq x \leq 3$ ;  $0 \leq y \leq 0.5$ ;



R = Lanthanides

J = Cr, Al, Ga, Co, Mn;

$0 \leq x \leq 3$ ;  $0 \leq y \leq 5$ ; and



$J_c = Bi, Tl, In, Au$ ;  $U_b = Na, K, Ag$ ;

$D_y = Pb, Sn, Ca, Cd, Ag, Sr, V$ ;  $U_f = Li$ ;

$D_z = Co, Fe, Ge, Ni, Mg, Zn$ ;

$J_n = Al, Co, Fe, Ga, Cr, Ti, Mn, V, Sb, Se$ ;

Q = Si, Sn, Ti, Mn, Ge, V, Nb, W;

$0 \leq c \leq 1$ ;  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$   $0 \leq b \leq 2$   $0 \leq z \leq 2$ ;

$0 \leq n \leq 3$ ;  $0 \leq w \leq 0.5$ ;  $0 \leq f \leq 1$ ;

where "U", "D", "R", "J", and "Q" are one or more: univalent, divalent, rare-earth, trivalent and tetravalent cations, respectively; and each lower-case letter of the formulae denotes a variable numerical value of the atomic ratio of that chemical element in the composition.

18. A transparent refractory oxide of claim 16.

19. A refractory oxide according to claim 16 which exhibits one or both of electrostatic and magnetic properties.

20. A refractory oxide of claim 18, wherein said oxide is  $\text{Al}_2\text{O}_3$ .

21. A refractory oxide of claim 18, wherein said oxide is  $\text{Al}_{1.998}\text{Cr}_{0.002}\text{O}_3$ .

22. A refractory oxide of claim 18, wherein said oxide is  $\text{Al}_{1.995}\text{Ti}_{0.005}\text{O}_3$ .

23. A refractory oxide of claim 18, wherein said oxide is  $\text{Al}_{1.988}\text{Nd}_{0.01}\text{Cr}_{0.002}\text{O}_3$ .

24. A refractory oxide of claim 18, wherein said oxide is  $\text{BaB}_2\text{O}_4$ .

25. A refractory oxide of claim 18, wherein said oxide is  $\text{Ba}_{1.9}\text{Na}_{1.05}\text{Nd}_{0.05}\text{Nb}_{3.26}\text{Ta}_{1.74}\text{O}_{15}$ .

26. A refractory oxide of claim 18, wherein said oxide is  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Nb}_2\text{O}_6$ .

27. A refractory oxide of claim 18, wherein said oxide is  $\text{BaTiO}_3$ .

28. A refractory oxide of claim 16, wherein said oxide is  $\text{Bi}_2\text{Si}_2\text{CaCu}_2\text{O}_8$ .

29. A refractory oxide of claim 18, wherein said oxide is  $\text{Bi}_2\text{Si}_{1.5}\text{O}_6$ .

30. A refractory oxide of claim 18, wherein said oxide is  $\text{KTa}_{0.63}\text{Nb}_{0.37}\text{O}_3$ .

31. A refractory oxide of claim 18, wherein said oxide is  $\text{Li}_{0.75}\text{Mg}_{0.13}\text{NbO}_3$ .

32. A refractory oxide of claim 18, wherein said oxide is  $\text{LiTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$ .

33. A refractory oxide of claim 18, wherein said oxide is  $\text{SrTiO}_3$ .

34. A refractory oxide of claim 18, wherein said oxide is  $\text{MgO}$ .

35. A refractory oxide of claim 18, wherein said oxide is  $\text{Pb}_2\text{KNb}_5\text{O}_{15}$ .

36. A refractory oxide of claim 16, wherein said oxide is  $\text{Y}_3\text{Fe}_5\text{O}_{12}$ .

37. A refractory oxide of claim 16, wherein said oxide is  $\text{YBa}_2\text{Cu}_3\text{O}_x$ .

38. A refractory oxide of claim 16, wherein said oxide is  $\text{YBa}_{5.63}\text{Cu}_{26.50}\text{O}_x$ .

39. A refractory oxide of claim 16, wherein said oxide is  $\text{YBa}_{5.67}\text{Cu}_{23.64}\text{O}_x$ .

40. A refractory oxide of claim 16, wherein said oxide is  $\text{YBa}_{5.5}\text{Cu}_{19.9}\text{O}_x$ .

41. A refractory oxide of claim 18, wherein said oxide is  $\text{ZnO}$ .

42. A refractory oxide of claim 18, wherein said oxide is  $\text{ZrO}_2$ .